near the melting point, and $[(T/T_m)-T_\infty/(T_m-T_\infty)]$ vanishes at $T=T_mT_\infty/(T_m-T_\infty)$, which is usually close to T_g. The result is that the entire second term in the brackets in Eq. (2) is negligible compared to T/T_m everywhere between T_m and T_g. Hence, we propose the relation

$$\Delta f=(\Delta h_f \Delta T/T_m)(T/T_m) \qquad (3)$$

to describe the change of driving force with temperature.

A numerical example will serve to show the accuracy of Eq. (3). It is assumed that the correct value of Δf in given by Eq. (1). For the case $T_m=500°K$, $T_g=325°K$, and $T_\infty=200°K$, the usual calculation of Δf, which omits the extra factor T/T_m, is 20% in error midway between T_m and T_g, and about 35% in error at T_g. For the same example, Eq. (3) yields Δf values that are virtually identical with the correct ones near T_m and T_g, and only a maximum of about 2% in error midway between T_m and T_g. Similar results are obtained with other reasonable examples.

[1] See, for example, M. Volmer, *Kinetic der Phasenbildung* (Theodor Steinkopff, Dresden and Leipzig, 1939).

Infrared Absorption Associated with Strong Hydrogen Bonds*

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SEVERAL investigators have proposed that there exists a more or less unique relation between the O—O distance in O—H—O hydrogen bonds and the shift of O—H vibrational frequency.[1–5] However, the meager intensities of some bands which have been ascribed to this vibration (notably in nickel dimethylglyoxime and potassium dihydrogen phosphate) have made us a little skeptical of the correlation in the case of very short, and possibly symmetrical, hydrogen bonds.

Recent x-ray investigations have disclosed several quite short hydrogen bonds in crystalline substances which have the possibility of being of the symmetrical type since, so far as the crystallographic evidence goes, the proton may well sit on a center of symmetry located between the two oxygen atoms. When investigating the infrared absorption of some of these substances we found no bands which we could attribute to the OH vibration at the frequencies predicted by the distance frequency relations mentioned above. At considerably longer wavelengths, however, we were struck by a remarkably intense background absorption. In both potassium hydrogen phenylacetate, reported to have an O—H—O distance of 2.54 A,[6,7] and in acetamide hemihydrochloride with the uniquely short distance of 2.40 A,[8] this absorption covers approximately the region 600–1600 cm^{-1}, rising to a maximum at about 800–900 cm^{-1}.

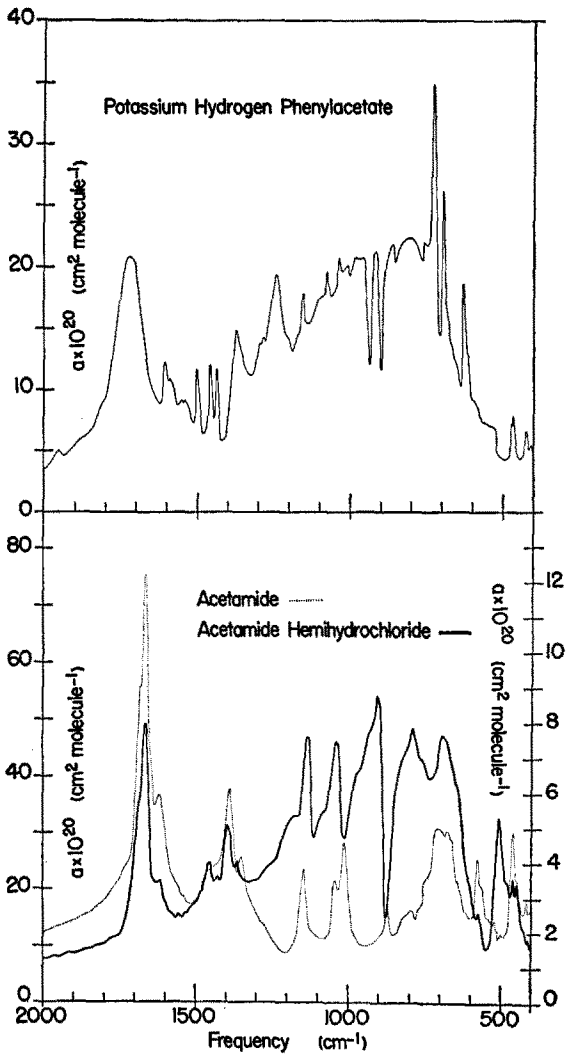

FIG. 1. Infrared absorption spectra of potassium hydrogen phenylacetate, acetamide, and acetamide hemihydrochloride between 400–2000 cm^{-1} in potassium bromide pressed disks. [Note: α is defined as $1/n \log_{10}(I_0/I)$, where n is the number of molecules per cm^2. In the lower section of the figure the scale at the left relates to $(CH_3CONH_2)_2 \cdot HCl$; at the right to CH_3CONH_2.]

In both cases the background absorption is overlaid with a number of maxima. In acetamide hemihydrochloride some of these correspond to weak absorptions in acetamide itself, which have, however, been very greatly intensified in the hemihydrochloride. More remarkable are the narrow and deep "windows" which appear in the background absorption. In acetamide hemihydrochloride the window rather suggests the anomalous dispersion effects sometimes observed in mull spectra. It may not be entirely accidental that it coincides with a weak *absorption* band in acetamide.

The spectra presented in Fig. 1 were obtained with KBr pressed disks which gave by far the best results.

All details of interest were, however, confirmed by mull spectra, though the substances in question gave unsatisfactory mulls which exhibited very degraded spectra. In the mull spectrum of potassium hydrogen phenylacetate shown by Hadži and Novak[9] it is very difficult to discern the features of real interest. Acetamide hemihydrochloride was examined also in KCl and KI matrices with essentially identical results.

Absolute measurements of intense absorption in solids are difficult to make and may well not have a very simple interpretation in the case of KBr matrices. In particular it is not always easy to distinguish between scattering and true absorption. Nevertheless if one naively compares the apparent integral extinction coefficients of acetamide and of its hemihydrochloride in the region 600–1600 cm^{-1} one finds an excess in the latter case which if one assumes that the reduced mass of the vibrating system is that of the proton, suggests the motion of considerably more than one proton charge. This may indicate that the frequencies of two or more of the three proton vibrations are nearly coincident, as indeed they are in the bifluoride ion in crystalline potassium bifluoride.[10]

It should be remarked that E. H. White has reported spectra for *N*-(*t*-butyl)-acetamide complexes with hydrohalic acids and the halogens,[11] both in the crystalline form and in chloroform solution, which are very similar to those which we observed in crystalline acetamide hemihydrochloride.

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Infrared Absorption Intensities of Hexafluorobenzene

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NOW that hexafluorobenzene is available[1] it seemed desirable that the intensities in its infrared absorption spectrum should be measured. The molecule has four active fundamentals, namely, the three in-plane e_{1u} modes and the out-of-plane a_{2u} mode. These have been assigned the values 1529, 1018+1003, 315, and 215 cm^{-1}, respectively, by Delbouille.[2] These frequencies are supported by a complete assignment by the present authors which will be presented elsewhere. The 1018 and 1003 bands are interpreted as a Fermi resonance doublet and are taken together for intensity measurement.

The intensities in the vapor phase of the higher bands were measured on a 2500 line per inch grating under conditions analogous to those for benzene itself[3] and the results are given in Table I. Only a qualitative value is available for the band at 315 cm^{-1}, namely, that it is about $\frac{1}{4}$ times the strength of the band at 1529 cm^{-1}. Force constants were chosen as far as possible to keep

Table I.

Frequency		Intensity
Observed	Calculated	Observed
1531	1531	$27.2\pm2.0\times10^{-7}$ cm^2 $molecule^{-1}$ sec^{-1} ln
1020, 1002	1006	$20.3\pm1.5\times10^{-7}$ cm^2 $molecule^{-1}$ sec^{-1} ln
315	312	$c.7\times10^{-7}$ cm^2 $molecule^{-1}$ sec^{-1} ln

the interaction constants similar to those in benzene[4]; in the nomenclature of Crawford and Miller[5] the values chosen were $\Gamma_4=0.991$; $\Lambda_4=3.701$; $\Omega_4=7.509$; $\mu_4=0.122$; $\tau_4=0.197$; $\xi_4=0.998\times10^5$ dyne/cm. This set of force constants predicts the calculated frequencies of Table I and was used to calculate the normal modes.

In the absence of exact measurements for the band at 315 cm^{-1} some further condition must be imposed before the dipole moment gradients can be derived. For benzene it was found experimentally[3] that the carbon stretching motion did not produce appreciable dipole moment provided the C—H links remained unchanged in direction. It is not unreasonable to assume that the corresponding result is true for hexafluorobenzene, i.e., that

$$\partial\mu/\partial S_{19}=3^{\frac{1}{2}}\cdot2^{-1}\rho\partial\mu/\partial S_{18}.$$

The relative sign ambiguity can be settled by invoking the approximate value of the 315-cm^{-1} band intensity. The alternative solutions predict 8 and 54 compared with the observed *c.*7 in 10^{-7} cm^2 $molecule^{-1}$ sec^{-1} ln units. Only the former is acceptable and the solution is $\partial\mu/\partial S_{18}=\pm2.2$, $\partial\mu/\partial S_{19}=\pm1.7$, $\partial\mu/\partial S_{20}=\mp8.7D/A$. Referred to individual C—F links the bond stretching moment gradient, $\partial\mu/\partial\Delta r=5.0D/A$ and the in-plane bending moment gradient, $\partial\mu/\partial\beta=1.6D$. The relative signs are such that if the fluorine is at the negative end of the bending dipole, then it behaves as if it carries a negative charge as regards the stretching gradient. The value of the stretching gradient is high, being one electron within experimental error, but it is not out of line with other fluorine containing bonds